A New Way to Deposit Organic Thin Films

Organic and polymer thin films will play a pivotal role in the development of next-generation electronic devices, passivation coatings, and chemical and biological sensors. However, in order to improve device and system performance and to meet future demands, new approaches are needed to grow thin films on wafer surfaces or small component areas with accurate thickness control. Depending on the particular application, one may want to deposit films containing single or multilayer structures of different organic or polymeric materials, homogeneous composite materials, or materials with graded compositions. In many situations, it will be necessary to deposit these materials discretely, achieve conformal coverage, and provide highly uniform films, especially with regard to surface coverage and thickness control.

For electronic- and optical-device applications, the materials of choice range from polymeric materials for fabrication and electrically stabilizing electronic components to organic dyes for nonlinear and optical-limiting applications. Thin films of polymeric, inorganic, and organic materials also play an important role in batteries, organic transistors, high-performance dielectrics, optical data storage and communications, and displays based on organic electroluminescent materials. Polymeric and lower molecular weight materials are essential as coatings for chemical and biochemical sensors. In the biomedical field, the use of polymers is important for applications ranging from passivation films for prosthetic devices to coatings for drug-delivery systems.

Thin-film deposition

Currently, thin films of organic and polymeric materials are processed by various techniques that differ in complexity and applicability. The selection of a deposition technique depends on the physicochemical properties of the material, the required film tolerances, the substrate to be coated, and the costs. The simplest methods of applying a thin organic film are solution casting, inkjet, aerosol, dip, and spin coating. In these techniques, a solution of coating material in a volatile solvent is dispersed on a substrate surface. When the solvent evaporates, it leaves behind a coating of the polymer.

Other techniques include in situ polymerization using plasma, electrochemical, catalytic, or photo-activated processes to coat directly onto the substrate surface. For certain classes of materials, thin films can be prepared by molecular-aggregation processes. In addition, processes such as vacuum sublimation, plasma deposition, and pulsed-laser deposition, or PLD (see *The Industrial Physicist*, September 1996, pp. 22–24), have been applied with limited success. However, despite the wide range of techniques by which thin films of organic and polymeric compounds can be deposited, the utility of each process is restricted to certain types of materials.

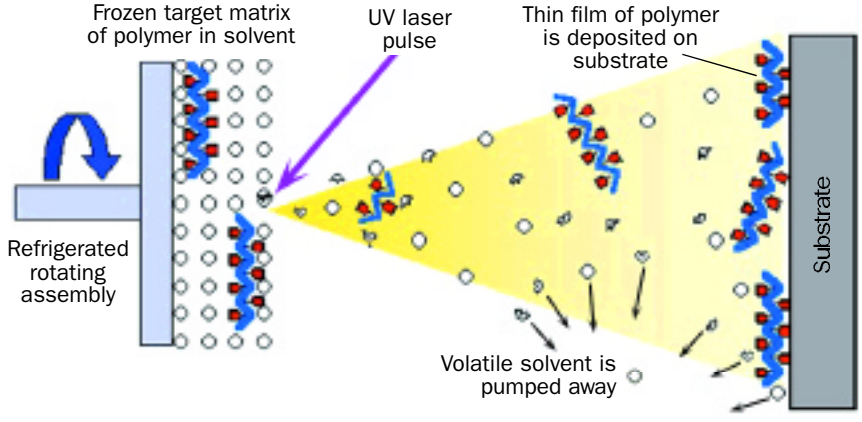

Figure 1. When a laser targets the frozen solution of organic material in a volatile solvent, the solute molecules are gently evaporated and deposited onto the substrate, and the solvent is pumped away.

In the search for a universal approach to producing high-quality thin films, a new vapor deposition technique, matrix assisted pulsed-laser evaporation (MAPLE), has emerged. The patented process, developed three years ago at the Naval Research Laboratory in Washington, DC, can generate high quality polymeric, organic, and biomaterial films on many types of substrates.

The technique has been used to deposit a wide range of organic and inorganic polymers, biopolymers, and low to intermediate molecular weight organics as thin, high-quality, uniform, and adherent coatings. These films are grown—with areas of a few square micrometers and in thicknesses ranging from 5 nm to several micrometers—over extended areas without degrading the physicochemical properties of the deposited materials.

Although the new process is similar to conventional PLD—both are vacuum-deposition techniques and they share many of the same advantages over traditional thin-film fabrication techniques—the new process has additional capabilities for depositing polymer thin films. First, the organic material arrives at the substrate surface free of solvating molecules, which eliminates solvent wetting and allows better control of coating placement. Second, the growth of multilayer structures of different compounds occurs without mixing at the layer interfaces, instead of the thin film of mixed materials that results from the solvent effects. And, unlike most traditional polymer or organic thin-film-fabrication techniques, MAPLE simultaneously deposits contamination-free films with monolayer thickness control (independent of the total thickness); requires minimal amounts of material; and provides enhanced film adhesion to the substrate. It is also easily combined with masking techniques (contact and noncontact).

To date, the technique has been used for processing thin films of polymeric and organic materials ranging from macromolecules as large as 600,000 amu, such as hydrogels, to small molecular species less than 200 amu, such as sugars. Furthermore, its ability to deposit films of complex polymeric and/or organic materials has been demonstrated for a wide variety of chemoselective polymers and plant and animal proteins, without damage to their structure or effect on their chemical or biological activity.

A gentler process

The key to the new process is the use of a frozen matrix as the laser target. This matrix, which consists of a dilute solution of a polymer or organic material in a volatile solvent, preferentially absorbs the laser pulse and allows the solute molecules to be gently desorbed from the target. At the molecular level, the technique is a photothermal process. Simply stated, the incident laser energy is absorbed by the bulk solvent molecules and converted into kinetic energy, which is then transferred to the embedded solute through collective collisions, resulting in the desorption of large molecular weight species. By carefully optimizing deposition conditions, this process takes place without significant decomposition or damage of the coating material. As in PLD, the laser pulse generates a forward directed vapor cone containing the evaporated material. When a substrate is positioned directly in this path, it is uniformly coated with the solute coating material while the volatile solvent molecules are removed by the chamber's vacuum pump, as shown in Figure 1.

In principle, the new process is similar to the chemical analytical technique called matrix assisted laser desorption-ionization mass spectrometry (MALDI-MS), a process developed for studying macromolecules to determine their molecular weight distributions. A significant difference between the two techniques lies in the treatment of the evaporated material. In the MAPLE process, the material of interest is not

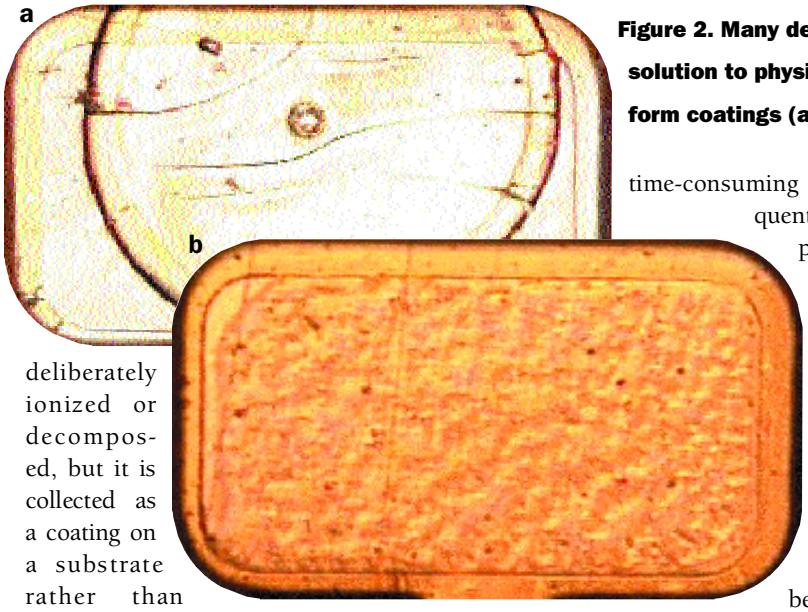

Figure 2. Many deposition techniques, such as ink-jetting, require a solution to physically wet the substrate, which results in less uniform coatings (a) than are obtained with the Maple process (b).

deliberately ionized or decomposed, but it is collected as a coating on a substrate rather than being directed into a mass spectrometer for further analysis.

A unique advantage of the emerging process is that it can be easily combined with noncontact shadow masks to limit the deposition to a required area. This is useful for coating fragile substrates, such as polymer coatings on atomic force microscope cantilevers, and is less expensive and less time-consuming than subsequent removal by patterning and etching. Patterns of polymers and organic materials with features on a 10-μm scale have been generated by MAPLE depositions through masks. This capability is important for the manufacture of sensor arrays and electronic components, in which the desired coating area is measured in micrometers.

Another advantage of the technique is that the polymer or organic material is deposited on a substrate free of bulk solvent. In contrast, deposition techniques such as aerosol, spin, ink-jet, and dip coating require a solution of the material in a solvent to physically wet the surface of a substrate. Such techniques limit the surface choices to materials that the solvent does not dissolve. The uneven and unpredictable wetting, distribution, and evaporation of the solvent molecules result in nonuniform coatings, as shown in Figure 2a. The superior quality of MAPLE-deposited films is apparent in Figure 2b.

Applications

There is considerable interest in thin-film processing of polymer and organic materials. In chemical and biochemical sensor applications, for example, the physicochemical properties of the chemoselective or bioselective coating are critical for sensor performance and quality control. Sensors with various chemoselective polymer coatings deposited by MAPLE have been found to perform better than the same devices coated by traditional techniques.

The technique may also play an important role in the deposition of thin, biocompatible polymer films for drug-delivery systems. In this application, highly uniform polymer films of specific thickness are required, either to form a diffusive layer that allows constant dosage of a drug through a skin patch or to encapsulate a drug in a biodegradable coating. Recently, MAPLE-deposited films of poly(lactic-*co*-glycolic) acid, a biodegradable polymer, were found to have the same molecular weight and structure as the starting material. These results hold promise for its use in depositing contiguous, nanometer-thick, biodegradable coatings that can be used to improve drug-delivery systems.

Composite thin films are another area of interest. One increasingly important structure is formulated as polymer–carbon nanotube composites. Processing these composite materials as thin films is complicated by nanotube agglomeration, polymer viscosity, and control over film thickness. Currently, studies are being conducted in which MAPLE is used to deposit homogeneous thin films of carbon nanotubes with or without a polymer matrix. As the scanning elec-

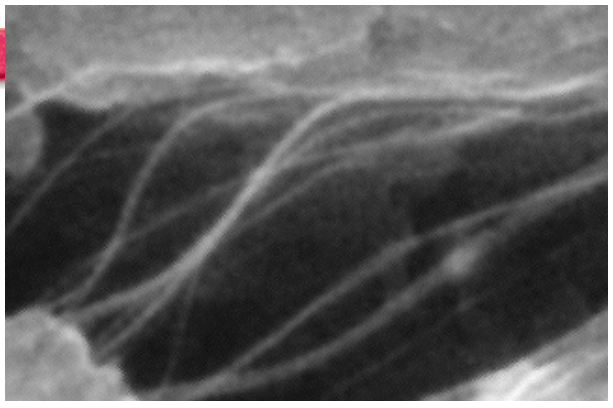

Figure 3. This scanning electron microscope image shows nanotubes distributed uniformly throughout a 1-µm-thick film of a poly(ethylene glycol)–carbon nanotube composite.

tron microscope image in Figure 3 shows, the process can deposit 1-µm-thick films of poly(ethylene glycol)–carbon nanotube composites. Although the carbon nanotubes in this photograph are aligned in the direction of the applied force during fracture, it is clear that they are uniformly distributed throughout the bulk of the thin film.

Finally, the new process has been used to deposit active proteins and other biomolecules, such as bovine insulin, horseradish peroxidase, myoglobin, and glucose oxidase. The activity of each enzyme or protein in the film has been verified, confirming the technique can deposit intact biomolecules.

Applications that require thin films of biomolecules include microfluidic biosensors, DNA and antibody microarrays, and biocompatible coatings for implants and pharmaceutical applications. For example, thin films of glucose oxidase, an enzyme used for glucose monitoring, have been deposited on the electrodes of miniature sensors. The resulting devices perform as well as those deposited by ink-jet techniques, with superior uniformity and coverage.

The wide range of materials that can be processed by MAPLE indicates the breadth of its potential applications. Bioapplications appear most promising, with encouraging early results in drug-delivery and release applications and with thin films of proteins. Other future applications may include the fabrication of unique polymer and organic multilayers with graded coatings, dense arrayed structures for sensor applications, light-emitting organics, bioelectronic interfacing, and novel microelectronics based on organic thin films.

The ability to fabricate high-quality organic coatings could affect many areas, such as electronics, flat-display technologies, microelectromechanical systems, biosensing, genomics, and tissue-based engineering. In addition, novel biomaterial structures could be fabricated for which there are no naturally occurring analogues.

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